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CHEMISTRY AND ANALYSIS OF THE PERMITTED COAL-TAR FOOD
DYES PONCEAU SX, SUNSET YELLOW FCF, AND BRILLIANT BLUE
FCF

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INTRODUCTION

Since the revision, in December, 1927, of Department Bulletin 1390 (2)¹ three new colors—ponceau SX, sunset yellow FCF, and brilliant blue FCF—have been approved and added to the list of permitted coal-tar food colors. The chemistry and special analytical methods for these three new dyes, as well as a revised method for lead, follow.

CHEMISTRY OF THREE NEW PERMITTED COLORS

PONCEAU SX

Ponceau SX, a monazo dye ($C_{18}H_{14}N_2O_7S_2Na_2$), is the disodium salt of the product obtained by coupling diazotized 1-amino-2,4-dimethylbenzene-5-sulphonic acid with 1-naphthol-4-sulphonic acid. These intermediates are used singly in other dyes listed in the Colour Index (11). The first component is the monosulphonic acid obtained by sulphonating asymmetric *m*-xylydine, 1-amino-2,4-dimethylbenzene, with 20 per cent oleum at temperatures in the neighborhood of 100° C. (Witt, G. P. 34,854, 1885 (14).) The *m*-xylydine is usually separated from crude xylydine as the acetate (G. P. 39,947, 1886 (10)). Nevile and Winther's acid, α -naphthol-4-sulphonic acid, the second component, is easily obtained of a satisfactory degree of purity (G. P. 46,307 (1) and G. P. 109,102 (3)).

Ponceau SX, when ground, is a red powder, easily soluble in water and dilute alcohol and slightly soluble in 95 per cent alcohol. The neutral aqueous solution is red, turning to a bluish red in high dilution. Addition of alkali changes the color to orange, and addition of acid causes a slightly more reddish tint. The dye dissolves in concentrated sulphuric acid, forming a bright cherry-red solution. When this solution is poured into water the dye partly precipitates and then redissolves.

¹ Italic numbers in parentheses refer to "Literature cited," p. 7.

The foundation and supplemental affidavits (12) should contain the analytical data for the determinations indicated in Table 1, which also gives the purity specifications.

TABLE 1.—*Specifications for ponceau SX*

Component	Maximum tolerance (ratio to pure coal-tar dye)	Minimum tolerance	Method of analysis ¹	Component	Maximum tolerance (ratio to pure coal-tar dye)	Minimum tolerance	Method of analysis ¹
	<i>Per cent</i>	<i>P. ct.</i>	<i>Page</i>		<i>Per cent</i>	<i>P. ct.</i>	<i>Page</i>
Moisture.....	10.0	-----	15	Iron.....	-----	-----	21
Insoluble matter:				Arsenic as As ₂ O ₃	.00014	-----	24
Total.....	.3	-----	15	Ether extractives:			
Nonvolatile.....	.2	-----	16	Neutral.....	(2)	-----	24, 25
Sodium chloride.....	5.0	-----	16, 18	Alkaline.....	(2)	-----	24, 25
Sodium sulphate.....	.5	-----	18	Acid.....	(2)	-----	24, 25
Sulphated ash.....	(2)	-----	19	Total.....	.2	-----	24, 25
Sodium in color.....	(3)	-----	19	Sulphur in color.....	(3)	-----	25, 26
Heavy metals.....	None.	-----	20	Color acid.....	-----	74.5	⁴ 26-28
Calcium.....	.3	-----	21	Pure coal-tar dye.....	-----	82.0	⁴ 26-28
Magnesium.....	.3	-----	21	Lower sulphonated dyes.....	5.0	-----	(9)
Aluminum.....	.1	-----	21				

¹ Given in U. S. Dept. Agr. Bul. 1390 (rev.) (2).

² Although no limit is defined here, a statement of the percentage found by analysis should be incorporated in the foundation and supplemental affidavits.

³ Theoretical.

⁴ As for ponceau 3R, etc.

⁵ Special method.

SUNSET YELLOW FCF

Sunset yellow FCF, a monazo dye (C₁₆H₁₀N₂O₇S₂Na₂), is the disodium salt of the product obtained by coupling diazotized sulphanilic acid with β -naphthol-6-monosulphonic acid (Schaeffer's acid) (B. P. 7,098, 1884 (13), and G. P. 32,964 (9)). These intermediates are used singly in numerous dyes listed in the Colour Index (11). The intermediates should be of such a state of purity and the coupling process and subsequent treatment so regulated that a minimum amount of the lower sulphonated dyes or subsidiary products is present in the finished dye.

The ground dye is an orange powder soluble in water and 50 per cent alcohol. The dye is slightly soluble in 95 per cent alcohol. The neutral solution is yellowish orange. Addition of alkali changes the tint to brownish red. Addition of acid produces almost no change. The powder dissolves in concentrated sulphuric acid with an orange color. This becomes yellow on dilution with water.

The foundation and supplemental affidavits (12) should contain the analytical data for the determinations indicated in Table 2, which also shows the purity specifications.

TABLE 2.—Specifications for sunset yellow FCF

Component	Maximum tolerance (ratio to pure coal-tar dye)	Minimum tolerance	Method of analysis ¹	Component	Maximum tolerance (ratio to pure coal-tar dye)	Minimum tolerance	Method of analysis ¹
	<i>Per cent</i>	<i>P. ct.</i>	<i>Page</i>		<i>Per cent</i>	<i>P. ct.</i>	<i>Page</i>
Moisture.....	10.0	-----	15	Iron.....	0.1	-----	21
Insoluble matter:				Arsenic as As ₂ O ₃	.00014	-----	24
Total.....	.3	-----	15	Ether extractives:			
Nonvolatile.....	.2	-----	16	Neutral.....	(²)	-----	24, 25
Sodium chloride.....	5.0	-----	16, 18	Alkaline.....	(²)	-----	24, 25
Sodium sulphate.....	.5	-----	18	Acid.....	(²)	-----	24, 25
Sulphated ash.....	(³)	-----	19	Total.....	.2	-----	24, 25
Sodium in color.....	(⁵)	-----	19	Sulphur in color.....	(²)	-----	25, 26
Heavy metals.....	None.	-----	20	Color acid.....		74	⁴ 26-28
Calcium.....	.3	-----	21	Pure coal-tar dye.....		82	⁴ 26-28
Magnesium.....	.3	-----	21	Lower sulphonated dyes.....	5.0	-----	(⁵)
Aluminum.....	.1	-----	21				

¹ Given in U. S. Dept. Agr. Bul. 1390 (rev.) (2).² Although no limit is defined here, a statement of the percentage found by analysis should be incorporated in the foundation and supplemental affidavits.³ Theoretical.⁴ As for Ponceau 3R, etc.⁵ Special method.

BRILLIANT BLUE FCF

Brilliant blue FCF, a triphenylmethane dye (C₃₇H₃₄O₉S₃N₂Na₂), is the disodium salt (Fierz' *Farbenchemie*, 4, p. 189) of the product obtained by condensing benzaldehyde-*o*-sulphonic acid with ethylbenzylaniline-sulphonic acid. As in the case of the other dyes of this type, pure intermediates are essential.

The following patents pertaining to the manufacture of the ammonium salt of this dye have been issued: United States patent 564801 (8); British patent 5068 (1896); German patents 88952 (5) and 89397 (7); and French patent 254742 (6). A complete description of the ammonium salt may also be found in the Colour Index (11) under No. 671, alphazurine FG.

Brilliant blue FCF is a dark purple bronzy powder which dissolves easily in water to form a greenish-blue solution. Addition of hydrochloric acid to the aqueous solution produces a green solution which changes to yellow upon further addition of acid. Alkali does not change the color of the cold solution, but a violet color is produced when the solution is boiled. The dye dissolves in concentrated sulphuric acid, forming a yellow solution which changes to green when diluted with water. The dye also dissolves in 95 per cent alcohol.

The methods of examination and the specifications for this dye are indicated in Table 3. The analytical data given here should be incorporated in the foundation and supplemental affidavits (12).

TABLE 3.—*Specifications for brilliant blue FCF*

Component	Maximum tolerance (ratio to pure coal-tar dye)	Minimum tolerance	Method of analysis ¹	Component	Maximum tolerance (ratio to pure coal-tar dye)	Minimum tolerance	Method of analysis ¹
	<i>Per cent</i>	<i>P. ct.</i>	<i>Page</i>		<i>Per cent</i>	<i>P. ct.</i>	<i>Page</i>
Moisture.....	10.0	-----	15	Aluminum.....	0.1	-----	21
Insoluble matter:				Iron.....	.3	-----	21
Total.....	.3	-----	15	Arsenic as As ₂ O ₃	.00014	-----	21-24
Nonvolatile.....	.2	-----	16	Ether extractives:			
Sodium chloride.....	3.0	-----	16-18	Neutral.....	(³)	-----	24, 25
Sodium sulphate.....	1.0	-----	19	Alkaline.....	(³)	-----	24, 25
Sodium acetate.....	3.0	(²)	19	Acid.....	(³)	-----	24, 25
Sulphated ash.....	(³)	-----	19	Total.....	.4	-----	24, 25
Sodium in color.....	(⁴)	-----	19	Sulphur in color.....	(⁴)	-----	25, 26
Heavy metals.....	None.	-----	20	Color acid.....	-----	77.4	26-28
Calcium.....	.3	-----	21	Pure coal-tar dye.....	-----	82.0	26-28
Magnesium.....	.3	-----	21	Subsidiary dyes.....	5.0	-----	(²)

¹ Given in U. S. Dept. Agr. Bul. 1390 (rev.) (2), as for light green SF yellowish.

² Special method.

³ Although no limit is defined here, a statement of the percentage found by analysis should be incorporated in the foundation and supplemental affidavits.

⁴ Theoretical.

SPECIAL ANALYTICAL METHODS

SODIUM ACETATE

For brilliant blue FCF.—Weigh 10 grams of the dye into a 200 c. c. Kjeldahl flask, add 25 c. c. of water, and connect the flask in an upright position to a vertical straight-tube water-jacketed condenser. Insert a separatory or dropping funnel through the stopper of the flask, together with the tube leading from the flask to the condenser. Add 15 c. c. of phosphoric acid (specific gravity 1.7) and heat the contents of the flask to boiling. Collect the acetic acid and condensed steam in a 300 c. c. Erlenmeyer flask to which has been added a standard solution of sodium hydroxide. Continue the boiling until about 250 c. c. has been distilled over, replacing the distillate by water from the dropping funnel so that the volume in the Kjeldahl flask remains about 20 c. c. This distillation should require about two hours. At the end of the distillation period, remove the receiver and titrate the excess alkali with standard acid, using phenolphthalein as indicator. Run a blank distillation and deduct the resulting acidity found. From the corrected acidity calculate the quantity of sodium acetate present in the dye.

LOWER SULPHONATED DYES

For ponceau SX and sunset yellow FCF.—To such a volume of a 1 per cent solution as contains 0.2 gram of dye, add 1 c. c. of concentrated hydrochloric acid and dilute to a volume of 50 c. c. Extract the lower sulphonated dyes by shaking the solution successively in three separatory funnels, each containing 50 c. c. of amyl alcohol. Wash the amyl alcohol extracts successively with 50 c. c. portions of 5 per cent salt solution until the washings are colorless. Dilute the amyl alcohol in each funnel with 100 c. c. portions of gasoline (specific gravity 0.65) and remove the lower sulphonated dyes by washing with several 10 c. c. portions of water. Determine the quantity of dye colorimetrically by comparison with a standard solution of the dye.

SUBSIDIARY DYES

For brilliant blue FCF.—Proceed as directed for light green SF yellowish (2, p. 31), except that after removal of the dye from the alcohol make the comparison with a standard solution of brilliant blue FCF and report as percentage of subsidiary dye.

LEAD

(Applicable to all permitted dyes)

REAGENTS

Ammonium acetate.—Dissolve 200 gm. of pure ammonium acetate $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$ in water and dilute to 500 c. c.

Dilute ammonium acetate solution.—Dilute 50 c. c. of the strong ammonium acetate to 500 c. c.

PROCEDURE

* Place 10 gm. of dye (15 gm. if necessary) in a tall 1,000 c. c. pyrex beaker, add 20 c. c. of concentrated nitric acid, and let boil. Then add 30 to 35 c. c. of concentrated sulphuric acid and continue the heating. Add small quantities of concentrated nitric acid at intervals until the organic matter is destroyed and the solution remains yellow or colorless when evaporated until sulphur trioxide fumes are freely evolved. Let cool and transfer the contents to a platinum dish. Continue the heating until the production of acid fumes decreases. If any carbon remains, moisten with a few drops of concentrated sulphuric acid and continue the heating. Finally, heat over the blast lamp or in a muffle furnace until fusion takes place, with the production of a clear liquid, free from bubbles.

Cool the dish and add about 5 c. c. of concentrated hydrochloric acid and evaporate until acid fumes can no longer be detected. Then add 2.5 c. c. of concentrated hydrochloric acid and about 20 c. c. of distilled water, and warm on the steam bath until all soluble matter goes into solution. Transfer to a 250 c. c. volumetric flask, dilute to the mark, and filter.

At this point a qualitative test for heavy metals should be made. For this purpose, place an aliquot part of the filtrate representing 1 gm. of dye in a test tube and saturate with washed hydrogen sulphide gas. Then place the test tube in a beaker containing boiling water and let it remain until the excess hydrogen sulphide has escaped. The presence of heavy metals is indicated if a dark precipitate settles out on standing. Place a 5 gm. aliquot portion of the filtrate in a tall 300 c. c. pyrex beaker, add about 3 c. c. of concentrated sulphuric acid, and evaporate until copious SO_3 fumes are evolved. Take up in 100 to 150 c. c. of water and add an equal volume of 95 per cent alcohol. Let stand overnight, filter through a small double filter (C. S. & S. 590),² and wash thoroughly with 50 per cent alcohol, using a wash bottle for the purpose.

Place the filter paper in a small beaker, add 20 c. c. of the strong ammonium acetate, and heat on the steam bath, breaking up the paper with a glass rod. Filter through a quantitative paper (C. S. & S. 590)² into a 50 c. c. volumetric flask and wash the paper and contents with dilute ammonium acetate until the filtrate reaches the mark.

² If desired, suitable fritted glass crucibles may be used for these filtrations.

Place an aliquot part³ of this solution in a colorimeter tube and dilute to a definite volume with distilled water. Then prepare standards⁴ containing known quantities of lead for comparison. To these add the same quantity of ammonium acetate as was used for the unknown and dilute to the same volume with water. Add a few drops of acetic acid, 1-1, to each and stir the contents well with glass rods. Then add 10 c. c. of freshly prepared hydrogen sulphide water to each tube and again stir the contents equally. Place the tubes over a white surface and estimate the quantity of lead by comparison with the standards.

Blanks.—Make a test for lead on the acids used, employing the procedure for the unknown here reported, 0.2 gm. of pure anhydrous sodium carbonate being added to the acids in order that the conditions obtaining in the blank may be somewhat similar to those in the unknown.

COLOR ACID AND PURE COAL-TAR DYE

For amaranth and ponceau 3R substitute the following method for that given in Department Bulletin 1390 (revised) (2).

For amaranth and ponceau 3R.—Proceed as for ponceau 3R, etc. (Bulletin 1390, 2, p. 28, par. 2), substituting 10 gm. of sodium citrate for sodium acid tartrate.

WATER EXTRACTIVES

The following optional method for determining water extractives may be used:

For yellow AB and yellow OB.—To determine the neutral extractives proceed as follows: Place 5 gm. of the well-powdered dye in a 300 c. c. separatory funnel and add 100 c. c. of benzene. Shake until the dye has dissolved. Extract with two 100 c. c. portions of water. Evaporate 100 c. c. of the extract in a weighed platinum dish on a steam bath. Dry in an oven at 100° to 105° C. Cool in a desiccator and weigh. Report the percentage increase in weight as neutral water extractives. Test small portions of the remainder of the extract for chlorides, sulphates, and nitrates. If more than traces are present, make the proper analyses on aliquot portions of the filtrate.

To determine the acid extractives, proceed as directed in Bulletin 1390 (2, p. 29, last paragraph), except that for "wash once with 25 c. c. of benzene," in line 5, substitute "wash with 25 c. c. portions of benzene until the benzene is practically colorless."

ANALYTICAL CONSTANTS

TABLE 4.—Sulphur, nitrogen, and sodium content

Color	Sulphur	Nitrogen	Sodium
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
Ponceau SX.....	13.35	5.83	9.57
Sunset yellow FCF.....	14.18	6.19	10.17
Brilliant blue FCF.....	12.13	3.53	5.80

³ In case very small quantities of lead are present, it will be necessary to use the 15 gm. charge of dye, so that a 10 gm. aliquot may be obtained.

⁴ From pure crystallized lead nitrate dried over sulphuric acid, prepare a standard solution containing 1 mgm. lead per c. c. From this solution prepare another solution containing 0.01 mgm. per c. c. and use this solution for preparing the standards. Make up this dilute solution just before it is to be used.

TABLE 5.—*Color acid equivalent to 1 c. c. of standard titanium trichloride*

Color	Molecular weight	Color acid equivalent to 1 c. c. 0.1 N titanium trichloride
Ponceau SX.....	<i>Grams</i> 436.26	<i>Gram</i> 0.010907
Sunset yellow FCF.....	408.24	.010206
Brilliant blue FCF.....	748.50	.03743

TABLE 6.—*Pure coal-tar dye equivalent to 1 c. c. of standard titanium trichloride*

Color	Molecular weight	Pure coal-tar dye equivalent to 1 c. c. 0.1 N titanium trichloride
Ponceau SX.....	<i>Grams</i> 480.25	<i>Gram</i> 0.016006
Sunset yellow FCF.....	452.22	.011305
Brilliant blue FCF.....	792.50	.03963

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